PART I
THE END-GROUP STRUCTURE OF POLYVINYL ALCOHOL

BY

GEORGE ESLER INSKEEP

B.S., Pennsylvania State College, 1940
M.S., University of Illinois, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1943

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INTRODUCTION

It has been shown that the polyvinyl alcohol chain possesses a regular 1,3-diol structure,[1] but the nature of the terminal grouping has not been studied. Several investigators have observed that interconversion between polyvinyl alcohol and its acetate, as well as certain treatments of polyvinyl alcohol, sometimes alter the apparent chain length as determined by viscosity measurement upon solutions of the polymers.[2] The purpose of the present research was to study these effects in detail and to discover whether this behavior could be traced to the presence of an aldehyde group at one end of the polyvinyl alcohol molecule.

DISCUSSION

Polyvinyl acetate was treated with sodium methoxide in methanol, or with sulfuric or hydrochloric acid in methanol, and the resulting polyvinyl alcohol was dissolved in water and reprecipitated in acetone. Reacetylation was accomplished with an excess of a two-to-one mixure of pyridine and acetic anhydride.

The following generalizations may be made:

(1) Alcoholysis of a medium- or short-chain polyvinyl acetate in anhydrous alkaline medium does not affect the apparent chain length.

(2) Alcoholysis of a medium- or short-chain polyvinyl acetate in anhydrous acid medium increases the chain length.

(3) Aqueous acid treatment of a polyvinyl alcohol produced by acid alcoholysis shortens the polymer chain; aqueous alkali does not change the length.

(4) Reflux of an acidic alcohol suspension of polyvinyl alcohol or aging of a solid polyvinyl alcohol containing traces of acid produces a longer chain.

(5) Reacetylation of the polyalcohol does not alter its length.

These results suggested the possibility that there is a terminal carbonyl group on the polyvinyl alcohol chain which can link it to an adjacent molecule through acetal formation with the hydroxyl groups. Such a group might arise from disproportionation or catalyst addition at the chain end during polymerization of the vinyl ester followed by saponification. Therefore polyvinyl alcohol was treated with 2,4-dinitrophenylhydrazine. The product showed a nitrogen content corresponding to one carbonyl group for each 372 monomer units; viscosity measurement gave a value for degree of polymerization of 331. Alcoholic alkali gave the reddish-violet color typical of nitrophenylhydrazones.[3] A comparison of absorption spectra in the near-ultraviolet region of this compound with those of the 2,4-dinitrophenylhydrazones of *n*-butyraldehyde and crotonaldehyde showed each to have a peak in the same vicinity; polyvinyl alcohol showed no peak in the region studied. The infrared absorption spectra of polyvinyl alcohol and its 2,4-dinitrophenylhydrazine derivative had two peaks in the carbonyl region,[4] one of which was lower in the spectrum from the derivative; this peak might have been caused by an aldehyde group or by residual water in the polymer films.

These facts indicate that there is probably an aldehyde group terminating the polyvinyl alcohol chain which leads to interchain acetal formation in acid environment in the absence of water.

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VITA

The author was born in Wilmington, Delaware, on December 25, 1918, and attended the Friends' school in that city and the public schools of Ishpeming, Michigan, and Magna, Utah; in June, 1936, he was graduated from the Roxbury High School in Succasunna, New Jersey. In September of that year he entered the Pennsylvania State College and in June, 1940, received the degree of Bachelor of Science in Chemical Engineering. The following September he began graduate study in organic chemistry at the University of Illinois, where he was granted the degree of Master of Science in June, 1941. He was holder of a fellowship from the Pennsylvania State College for the year 1940-41, was a teaching assistant from September, 1941, until February, 1943, and was Du Pont Fellow from February to June, 1943.

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